

ENHANCEMENT OF MOLECULAR WEIGHT OF L-LACTIC ACID POLYCONDENSATES UNDER VACUUM IN SOLID STATE

POVEČANJE MOLEKULARNE TEŽE POLIKONDENZATOV L-LAKTIČNE KISLINE V TRDNEM STANJU Z VAKUUMOM

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Prejem rokopisa – received: 2011-06-05; sprejem za objavo – accepted for publication: 2011-07-18

Enhancement of L-lactic acid polycondensates by involving of postpolycondensation reactions in solid state under vacuum and catalyzed by stannous 2-ethylhexanoate were studied in the presented work. The catalyst was used only in postpolycondensation step. An effect of the catalyst concentration and postpolycondensation reaction time on resulting properties of poly(lactic acid) was studied by gel permeation chromatography, Fourier transform infrared spectroscopy and differential scanning calorimetry. Results show significant enhancement of molecular weight in case of the systems containing 2 wt. % of the catalyst due to the postpolycondensation procedure ($M_w \sim 91.0$ kg/mol; i.e. 1655 % after 24 hours). However, further progress can be assumed with increasing reaction time. This enhancement of poly(lactic acid) molecular weight had a response corresponding to changes of both physico-chemical and thermal properties of the solid state postpolycondensation products.

Keywords: poly(lactic acid), solid state postpolycondensation, molecular weight enhancement

V tem delu smo za izboljšanje lastnosti polikondenzata L-laktične kisline raziskali vpliv postpolikondenzacijskih reakcij v trdnem stanju z vakuumom. Za katalizo smo v post polikondenzacijskem koraku uporabili katalizator kositrov 2-etilheksanoat. Vpliv koncentracije katalizatorja in časa postpolikondenzacijskih reakcij na lastnosti poli(laktične kisline) smo raziskovali z gel prepustno kromatografijo, fourierjevo transformacijsko infrardečo spektroskopijo in z diferenčno dinamično kalorimetrijo. Zaradi postpolikondenzacijskega postopka smo opazili bistveno povečanje molekulske mase v sistemu, kje smo uporabili 2 ut.% katalizatorja ($M_w \sim 91.0$ kg/mol; 1655 % po 24 urah). Še dodatno povečanje bi najverjetneje lahko dosegli tudi s podaljšanjem časa reakcije. Izkazalo se je, da ima povečanje molekulske mase poli(laktične kisline) vpliv na fizikalno-kemijske, kot tudi na termične lastnosti trdnih postpolikondenzacijskih produktov.

Ključne besede: poli(laktična kislina), postpolikondenzacija trdnega stanja, izboljšanje molekulske teže

1 INTRODUCTION

Poly(lactic acid) (PLA) is one of the biodegradable polymers with promising applicability in the field of environmentally friendly materials production (e.g. packaging, disposable items) as well as in medicine (medical devices, drug carriers).¹⁻⁷ Generally, PLA can be synthesized by three basic ways; (i) ring opening polymerization; (ii) azeotropic distillation in solution; (iii) polycondensation in molten state.^{8,9} First two methods are known to be experimentally difficult due to sensitivity to presence of impurities. The lastly mentioned method allows relatively low-demanding PLA preparation.^{10,11} However, it is redeemed by low molecular weight of the polycondensation products, which is not acceptable for most of the engineering applications.¹²

The disadvantage of the low molecular weight polycondensation product can be offset by introduction of subsequent techniques – postpolycondensation reactions, which can yield a product with high molecular weight. Basically, two approaches have been known. The first one represents coupling reactions between functional

groups intentionally introduced at the end of PLA chains (e.g. hydroxyl) and bifunctional compound (e.g. diisocyanate).¹³ The second method involves reaction between ends of the PLA chains and/or residual monomer, which is usually carried out in solid state under specific conditions.⁸ This postpolycondensation reaction is analogy to the method developed for molecular weight increasing of poly(ethylene terephthalate)¹⁴, which has been also studied for an usage in medical applications.¹⁵⁻¹⁷ The advantage of this method is fact that an addition of external chemical agents is not required.

There are several works describing solid state postpolycondensation of PLA. For instance, Zhang et al. reported two step (melt/solid) preparation of high molecular weight PLA.¹⁸ Effect of crystallization on the solid state polycondensation of PLA was investigated by Xu et al.¹⁹ These both works apply SnCl₂ as a catalyst for PLA prepolymer preparation and additional catalyst for postpolycondensation reaction. The resulting products had molecular weight in the range 20-150 kg/mol. Polydispersity index was mostly tightly below 2. However, to the best of our knowledge, solid state postpolycondensation of low molecular weight PLA prepared by

direct polycondensation of L-lactic acid without using of a catalyst has not been studied.

This work is dedicated to investigation of solid state postpolycondensation of low molecular weight L-lactic acid polycondensates prepared by non-catalyzed reaction. Various concentration of an organotin based compound was used for catalysis of the postpolycondensation step subsequently. Resulting products were characterized by gel permeation chromatography; differential scanning calorimetry and Fourier transform infrared spectroscopy.

2 EXPERIMENTAL PART

2.1 Materials

L-lactic acid (LA) $C_3H_6O_3$, 80 % water solution, optical rotation $\alpha = 10.6^\circ$ (measured by the polarimeter Optech P1000 at 22 °C, concentration of 10 %) was purchased from Lachner Neratovice, Czech Republic. Stannous 2-ethylhexanoate ($Sn(Oct)_2$) (~95 %) was supplied by Sigma Aldrich, Steinheim Germany. The solvents acetone C_3H_6O , chloroform $CHCl_3$ and methanol CH_4O (all analytical grade) were bought from IPL Lukes, Uhersky Brod, Czech Republic.

2.2 Sample preparation

The procedure as samples preparation is summarized in **Figure 1**. Generally, PLA prepolymer was prepared by direct melt polycondensation of L-lactic acid. A typical procedure was as follows: 50 ml lactic acid solution was added into a double necked flask (250 ml) equipped with a Teflon stirrer. The flask was then placed in an oil bath heated by magnetic stirrer with heating and connected to a laboratory apparatus for distillation under reduced pressure. The dehydration step followed at 160

°C, reduced pressure 15 kPa for 4 hours. The flask with dehydrated mixture was connected to the source of vacuum (100 Pa) and the reaction continued for 24 hours at the temperature 180°C. The resulting product was allowed to cool down at room temperature and then dissolved in acetone. The polymer solution was precipitated in a mixture of chilled methanol/distilled water 1:1 (v/v). The obtained product was filtrated, twice washed with hot distilled water (80 °C) and dried in at 55 °C for 48 hours under the pressure 15 kPa.

Solid state postpolycondensation was proceeded as follows: 6 g of the prepolymer was dissolved in 20 ml of toluene and the catalyst was added to the polymer solution (0.5, 1 and 2 wt. %). The solvent was evaporated at elevated temperature (80 °C) and the residuals were dried for 6 hours at 50 °C and 3 kPa. After that the prepolymer containing the catalyst was placed into a test tube and crystallized at 105 °C for 1 hour. Finally, the test tubes were connected to the vacuum source (100 Pa). The sampling was done after 6, 12, 18 and 24 hours.

2.3 Characterization of samples

2.3.1 Determination of molecular weight by gel permeation chromatography (GPC)

GPC analyses were performed using a chromatographic system Breeze (Waters) equipped with a PLgel Mixed-D column (300 × 7.8) mm, 5 μm (Polymer Laboratories Ltd). For detection, a Waters 2487 Dual absorbance detector at 254 nm was employed. Analyses were carried out at room temperature with a flow rate of 1.0 mL/min in chloroform. The column was calibrated using narrow molecular weight polystyrene standards with molar mass ranging from 580 g/mol to 480 000 g/mol (Polymer Laboratories Ltd). A 100 μL injection loop was used for all measurements. The sample concentration ranged from 1.6 mg/mL to 2.2 mg/mL. Data processing was carried out using the Waters Breeze GPC Software (Waters). The weight average molar mass M_w , number average molar mass M_n and Polydispersity ($PDI=M_w/M_n$) of the tested samples were determined. Relative enhancement of M_w (EM_w) was calculated according as follows:

$$EM_w (\%) = \frac{M_{wS}}{M_{w0}} \times 100 \quad (1)$$

where M_{wS} represents M_w of the sample and M_{w0} is M_w of the prepolymer.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

Functional groups in LA polycondensation products were identified using FTIR analysis. The investigation was conducted on Nicolet 320 FTIR, equipped with attenuated total reflectance accessory (ATR) utilizing Zn-Se crystal and the software package "Omnic" over the range of 4000-650 cm^{-1} at room temperature. The uniform resolution of 2 cm^{-1} was maintained in all cases.

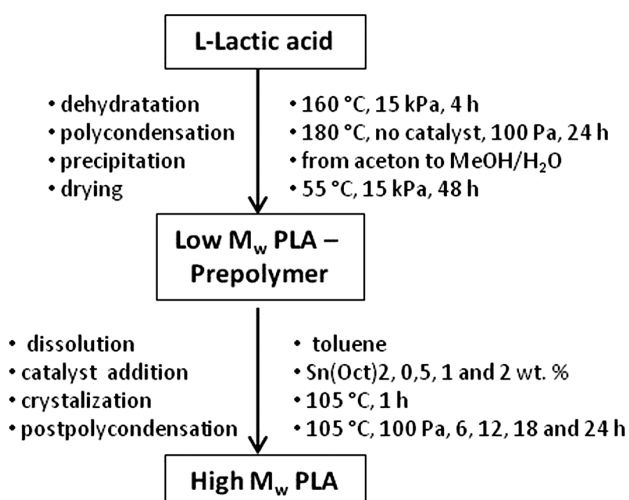


Figure 1: Scheme of two step preparation of high M_w PLA through the postpolycondensation reaction in solid state

Slika 1: Shema dvostopenjske priprave visoko M_w PLA z uporabo postpolikondenzacijskih reakcij v trdnem stanju

2.3.3 Differential scanning calorimetry (DSC)

For the determination of glass transition temperature T_g , melting point T_m the differential scanning calorimetry was used. Approximately 8 mg of the sample were placed in an aluminium pan, sealed and analyzed on Mettler Toledo DSC1 STAR System under nitrogen flow (20 cm³/min). The analysis was carried out according to the following programme: (i) first heating scan 0 – 195 °C (10 °C/min); (ii) annealing at 195 °C for 1 minute; (iii) cooling scan 195 – 0 °C (10 °C/min); (iv) annealing at 0 °C for 1 minute; (v) second heating scan 0 – 195 °C (10 °C/min). Melting point temperature (T_m) was obtained from the first heating cycle. The value of glass-transition temperature (T_g) was determined in the second heating scan at the midpoint stepwise increase of the specific heat associated with glass transition. The DSC results for prepolymer and the sample after 24 hours of postpolycondensation reaction are presented in this work.

3 RESULTS AND DISCUSSION

The results obtained from GPC analysis are summarized in **Table 1**. The prepolymer (see the scheme in **Figure 1**) had $M_w = 5.5$ kg/mol and low PDI . It shows relatively narrow distribution of molecule chain lengths. Subsequently proceeded postpolycondensation reactions led to enhancement of M_w . However, significant increase in M_w was observed mostly after 18 hours of the reaction. Further prolongation of the reaction time (24 hours) had positive effect on M_w enhancement as well as addition of the catalyst ($\text{Sn}(\text{Oct})_2$). It can be noticed in **Figure 2** where dependence of relative enhancement of M_w , EM_w , (Equation 1) is depicted as a function of postpolycon-

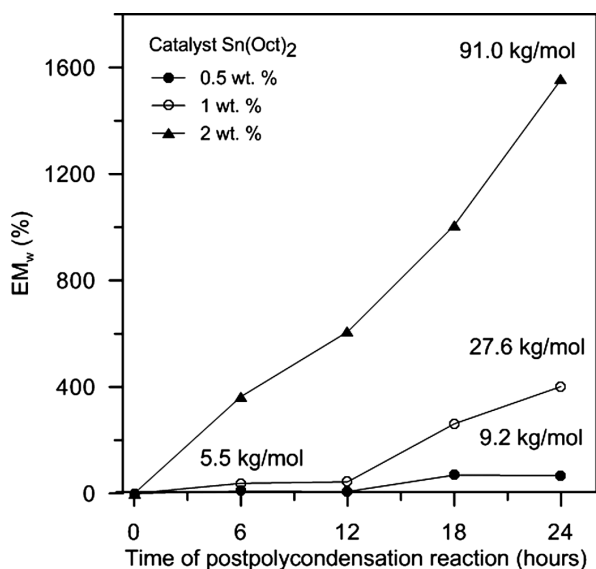


Figure 2: Relative enhancement of M_w versus time of postpolycondensation reaction in presence of various catalyst concentrations

Slika 2: Relativno povečanje M_w glede na čas polikondenzacijskih reakcij in v prisotnosti katalizatorja pri različnih koncentracijah

densation reaction time for various concentration of the catalyst. The lowest investigated concentration of the catalyst seemed to be not suitable for high M_w PLA preparation. Maximal EM_w was only 167 % in this case (9.2 kg/mol). Better results were noticed for the systems containing 1 wt. % of the catalyst. EM_w was 502 % after 24 hours of the postpolycondensation reaction. However, it represents $M_w = 27.6$ kg/mol, which is still not considerable as high M_w product. Significantly different results were observed when the concentration of the catalyst was risen to 2 wt. %. As can be seen in **Figure 2**, EM_w for this system was higher already after 12 hours of postpolycondensation reaction that those described above (0.5 and 1 wt. %, 24 hours). In addition, its EM_w steeply increases with the reaction time. The sample after 24 hours of the reaction showed $EM_w = 1655$ %. It corresponds to 91.0 kg/mol. PDI was 1.6. It reveals narrow distribution of the chain lengths.

Table 1: GPC characteristics of the prepolymer and the samples after various times of postpolycondensation reaction

Tabela 1: GPC karakteristika predpolimera in vzorcev z različnimi časi postpolikondenzacijskih reakcij

Catalyst concentration (wt. %)	Time of postpolycondensation reaction (hours)				
	0*	6	12	18	24
0.5	M_w/PDI^{**}	M_w/PDI	M_w/PDI	M_w/PDI	M_w/PDI
1	5.5/1.68	7.6/1.6	7.9/2.1	19.9/2.2	27.6/1.7
2		25.5/2.6	38.9/2.6	60.9/2.9	91.0/1.6

* prepolymer

** M_w – weight average molecular weight (kg/mol), PDI – polydispersity

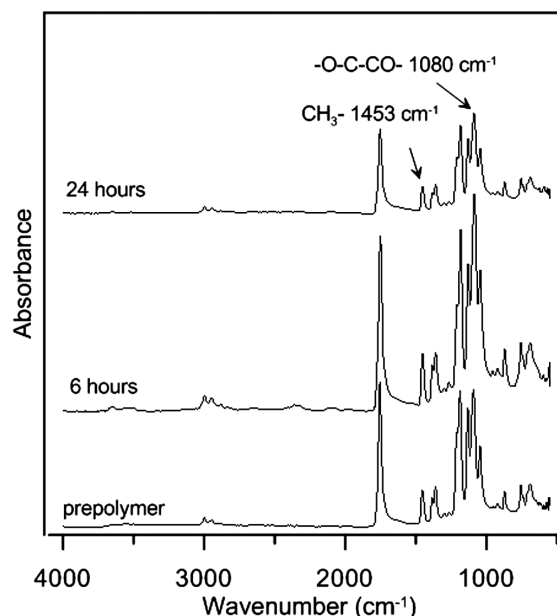


Figure 3: FTIR-ATR spectra of PLA prepolymer and products after 6 and 24 hours of postpolycondensation reaction (catalyzed by $\text{Sn}(\text{Oct})_2$, 2 wt. %)

Slika 3: FTIR-ATR spekter PLA predpolimera in produktov po 6 in 24 urah postpolikondenzacijskih reakcij (katalizirano z 2 ut. % $\text{Sn}(\text{Oct})_2$)

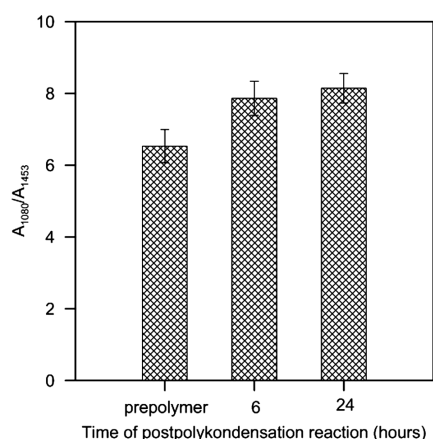


Figure 4: Normalized areas of the FTIR-ATR absorption peaks at 1080 cm^{-1} of PLA prepolymer and products after 6 and 24 hours of postpolycondensation reaction (catalyzed by $\text{Sn}(\text{Oct})_2$, 2 wt. %)

Slika 4: Normalizirana površina FTIR-ATR adsorpcijskih vrhova pri 1080 cm^{-1} PLA predpolimera in produktov po 6 in 24 urah postpolikondenzacijskih reakcij (katalizirano z 2 ut. % $\text{Sn}(\text{Oct})_2$)

The process of postpolycondensation of PLA was also investigated by FTIR-ATR analysis. **Figure 3** shows FTIR-ATR spectra of PLA precursor and the samples after 6 and 24 hours of postpolycondensation reaction in presence of 2 wt. % of the catalyst. A detailed description of PLA FTIR spectra can be found, for example, in our previous works.^{11,12} From the observation of the postpolycondensation reaction point of view, it is interesting to focus on formation of new ester bonds, reduction of carboxylic and hydroxyl groups. Due to complexity of the PLA FTIR spectra, the most convenient could be the firstly mentioned ester bonds formation, which could be characterized by absorption at 1080 cm^{-1} .²⁰ Areas of this absorption peak, A_{1080} , were normalized on the peak area representing absorption of

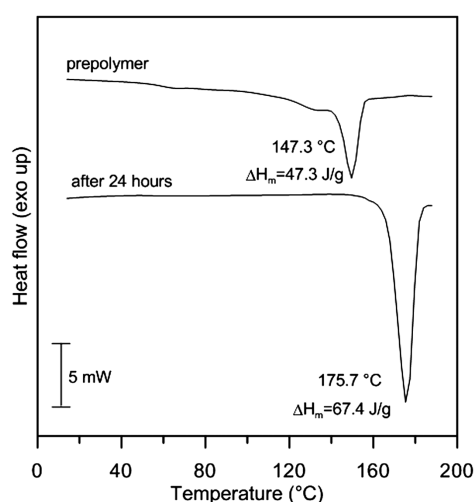


Figure 5: DSC curve (first heating scan) of PLA prepolymer and products after 24 hours of postpolycondensation reaction (catalyzed by $\text{Sn}(\text{Oct})_2$, 2 wt. %)

Slika 5: DSC krivulja (prvo gretje) PLA predpolimera in produktov po 24 urah postpolikondenzacijskih reakcij (katalizirano z 2 ut. % $\text{Sn}(\text{Oct})_2$)

methyl groups at 1453 cm^{-1} (A_{1453}). Dependence of A_{1080}/A_{1453} versus time of the postpolycondensation reaction is depicted in **Figure 4**. It can be seen that concentration of ester bonds increases with rising time of the reaction. It is in agreement with the GPC results.

The significant enhancement of M_w described above affects properties of the resulting PLA including thermal behavior of the polymer. **Figure 5** shows DSC spectra (first heating scan) of the prepolymer and PLA postpolycondensation product obtained after 24 hours in presence of 2 wt. % of the catalyst. It can be noticed that increasing M_w of the PLA samples (see **Table 1**) led to significant shift of the T_m towards higher values (from 147.3 to $175.7\text{ }^\circ\text{C}$). Enthalpy of melting, ΔH_m , was 47.3 and 67.4 J/g , respectively (**Figure 5**). It means that a content of crystalline phase in the treated samples increased noticeably (from 50.5 to 71.9% , $\Delta H_{m0} = 93.7\text{ J/g}$)²¹ due to postpolycondensation reaction connected with rising of M_w . In addition, glass transition temperature, T_g , (taken from the second heating scan – not shown here) was also increased from $45.2\text{ }^\circ\text{C}$ (PLA precursor) to $53.6\text{ }^\circ\text{C}$ (after 24 hours of the reaction, 2 wt. % of the catalyst). These observations together with the GPC results reveal linear structure of the PLA macromolecules while the postpolycondensation process takes place at the end of the PLA precursor chains in the amorphous phase region⁸.

4 CONCLUSIONS

This work was dedicated to investigation of the high molecular weight poly(lactic acid) (PLA) synthesis through multistep process including postpolycondensation reactions in solid state. Unlike other already published works in this field, presented work involves using of catalyst (stannous 2-ethylhexanoate) only in postpolycondensation step. The main attention was paid to determination of the catalyst concentration and time of the postpolycondensation reaction on the molecular weight of the resulting products by using gel permeation chromatography. It was correlated with the results from Fourier transform infrared spectroscopy and differential scanning calorimetry.

The results show that the role of the catalyst concentration is crucial to enhancement of molecular weight of the PLA during the solid state postpolycondensation process. While low concentration of the catalyst (up to 1 wt. %) do not provide sufficient results (enhancement up to 502 % after 24 hours), systems containing 2 wt. % of the catalyst showed noticeably higher molecular weight enhancement – 1655 % (from 5.5 to 91.0 kg/mol). Another important parameter is time of the postpolycondensation step. Obtained results reveal a possibility of an additional enhancement of PLA molecular weight for the postpolycondensation reaction times above 24 hours. However, finding of a time optimum must be further investigated.

Acknowledgements

This research was financially supported by the Ministry of Education, Youth and Sports of the Czech Republic (project No. 2B08071 and ME09072) and Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF, project No. CZ.1.05/2.1.00/03.0111).

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